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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Inventor(s): FORREST et al.

Serial No.: 10/026,091

Filing Date: December 21, 2001

For: ORGANIC PHOTOSENSITIVE  
OPTOELECTRONIC DEVICES WITH  
TRANSPARENT ELECTRODES

Art Unit: Not yet assigned

Examiner: Not yet assigned

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4-22-00

**Assistant Commissioner for Patents**

Washington D.C. 20231

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Signature: Kevin T. Godlewski  
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**PRELIMINARY AMENDMENT**

SIR:

Please amend the above-identified application before examination as follows.

**In the Specification:**

On page 1, line 3 (after the title), please insert the following:

**--CROSS-REFERENCE TO RELATED APPLICATION**

*AL*  
This application is a continuation of co-pending Patent Application No. 09/136,342, filed  
August 19, 1998--

Please replace the paragraph beginning on page 14, line 25, with the following:

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*A2*

--The present invention is directed to organic photosensitive optoelectronic devices utilizing transparent electrodes, in particular, devices that include an organic photosensitive optoelectronic cell comprised of at least one pair of two transparent electrodes, that is, a transparent cathode and a transparent anode, or devices that have a transparent electrode in superposed relationship upon the top surface of a substrate with at least one photoconductive organic layer disposed between the electrode and the substrate. More specifically, the organic photosensitive optoelectronic devices of the present invention may be comprised of a transparent cathode that is highly transparent and/or highly efficient. As representative embodiments, such transparent cathodes may be the highly transparent, highly efficient and/or low resistance non-metallic or metallic/non-metallic composite cathodes, such as disclosed in the co-pending applications 08/964,863 (hereinafter "Parthasarathy Appl. '863") and 09/054,707 (hereinafter "Parthasarathy Appl. '707") or in Forrest '436, each of which being incorporated in its entirety by reference.--

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Please replace the paragraph starting on page 19, line 1 with the following:

*A3*

--Taking into account that the additional subcells of the stacked device tend to introduce additional losses, such as that due to the residual reflectivity of the transparent electrodes, the maximum external quantum efficiency that can be achieved for a fully optimized stacked device would typically be somewhat less than the internal quantum efficiency of an optimal subcell. Nevertheless, using the methods of the present invention for optimizing the external quantum efficiency of an organic photosensitive optoelectronic device, substantially higher external quantum efficiencies may be achieved for a stacked device than are possible for a device having a single cell, which is optimized for external quantum efficiency at the expense of internal quantum efficiency.--

Please replace the paragraph starting on page 19, line 24 with the following:

*A4*

--When the term "subcell" is used hereafter, it may refer to a organic photosensitive optoelectronic construction of the unilayer, bilayer or multilayer type. When a subcell is used individually as a photosensitive optoelectronic device, it typically includes a complete

set of electrodes, i.e., positive and negative. As disclosed herein, in some stacked configurations it is possible for adjacent subcells to utilize common, i.e., shared, electrode or charge transfer layers. In other cases, adjacent subcells do not share common electrodes or charge transfer layers. The term "subcell" is disclosed herein to encompass the subunit construction regardless of whether each subunit has its own distinct electrodes or shares electrodes or charge transfer layers with adjacent subunits. Herein the terms "cell", "subcell", "unit", "subunit", "section", and "subsection" are used interchangeably to refer to a photoconductive layer or set of layers and the adjoining electrodes or charge transfer layers. As used herein, the terms "stack", "stacked", "multisection" and "multicell" refer to any optoelectronic device with multiple layers of a photoconductive material separated by one or more electrode or charge transfer layers.--

Please replace the paragraph starting on page 23, line 30 with the following:

~~--The preferred embodiments of the present invention include, as one or more of the transparent electrodes of the optoelectronic device, a highly transparent, non-metallic, low resistance cathode such as disclosed in Parthasarathy Appl. '707, or a highly efficient, low resistance metallic/non-metallic composite cathode such as disclosed in Forrest '436. Each type of cathode is preferably prepared in a fabrication process that includes the step of sputter depositing an ITO layer onto either an organic material, such as copper phthalocyanine (CuPc), PTCDA and PTCBI, to form a highly transparent, non-metallic, low resistance cathode or onto a thin Mg:Ag layer to form a highly efficient, low resistance metallic/non-metallic composite cathode. Parthasarathy Appl. '707 discloses that an ITO layer onto which an organic layer had been deposited, instead of an organic layer onto which the ITO layer had been deposited, does not function as an efficient cathode.--~~

Please replace the paragraph starting on page 27, line 4 with the following:

~~--In an exemplary embodiment of the present invention, as shown in Fig. 3, the device structure 300 is deposited onto an insulating substrate 301. First electrode 302 is transparent and comprises, e.g., ITO deposited by conventional techniques or available predeposited on~~

commercial substrates to an approximate thickness of 1000-4000 Å, preferably less than 2000 Å and most preferably around 1000 Å. Layer 303 is a single organic photoconductor, e.g., CuPc or PTCDA, or PTCBI deposited by organic molecular beam deposition (OMBD) in a layer of thickness 300-1000 Å, preferably about 500 Å. Second electrode 304 is transparent, e.g., ITO deposited by sputtering to an approximate thickness of 1000-4000 Å, preferably less than 2000 Å and most preferably around 1000 Å. An understanding from the prior art would indicate that such a symmetric *unilayer* device configuration would not generate a net photocurrent. However, the necessary asymmetry is believed to arise at the interface between organic photoconductor layer 303 and second electrode 304 from electronic surface states in organic photoconductor layer 303 produced during the deposition of ITO second electrode 304. The damage region is schematically represented as region 303a. The exact mechanism by which the altered region at the interface produces asymmetric charge separating regions is not completely understood. Without limiting the present invention to a particular theory, the effect of energetic electrode deposition, such as sputtering, may be sufficient to alter the energy states at the interface so significantly that the conventional picture of opposing mirror-image Schottky barriers is altered. Parthasarathy Appl. '707 discloses that the surface states, which may be defects, may effectively provide small energy "steps" that allow electrons to more easily traverse what would otherwise be, for example, a Schottky barrier. One theory of unilayer device operation is that deposition of electrode 304 onto organic layer 303 creates a low resistance contact, here a cathode. It is believed in this case that the resulting asymmetry would yield a net photocurrent.--

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Please replace the paragraph starting on page 28 at line 20 with the following:

--Embodiment 4A00 incorporates the low resistance metal substitute cathode disclosed in Parthasarathy Appl. '707. It should be observed that in contrast to the OLEDs of Parthasarathy Appl. '707 wherein the electrons move from the cathode into the adjacent organic semiconductor, organic photosensitive optoelectronic bilayer device 400 represents an embodiment of a photosensitive optoelectronic device. Accordingly, the thicknesses of the photoconductive organic materials are adjusted to the requirements of a photosensitive

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optoelectronic device, and during operation electrons flow from second organic layer 404 into second electrode 4A05. Without being limited to this particular theory, it was typically believed by one skilled in the art that metal substitute electrodes, e.g., ITO, would create a barrier to electron flow in both directions, i.e., into or out of the device, when such materials were used as cathodes. The low resistance operation of the ITO cathode in the present invention demonstrates that the surface states proposed in Parthasarathy Appl. '707 are effective in reducing the barrier to electron flow in either direction at an ITO cathode made in accord with the present invention of Parthasarathy Appl. '707. Although first organic layer 403 and second organic layer 404 may be interchanged in some cases and still obtain a working device with only a reversal of polarity, these embodiments are less preferred due to the reduced efficiency of a device whenever the metal substitute electrode is used as the bottom cathode. The surface states believed to effectively reduce the barrier at an ITO cathode are not thought to be produced when the organic thin film is deposited onto the ITO layer. The term "low resistance metal substitute cathode" is, thus, used herein to refer to a metal substitute, e.g., ITO, prepared by sputter depositing a metal substitute, e.g., ITO, onto an organic layer, in particular, as distinct from an electrode prepared by depositing an organic layer onto a metal substitute, e.g., ITO. It is believed herein that the barrier-reducing effect of surface states also can function to permit holes to traverse what would otherwise be blocking junctions at an interface between an organic semiconductor layer and an electrode or charge transfer layer.--

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Please replace the paragraph starting on page 30 at line 17 with the following:

--In the bilayer cells any rectifying effect of the organic material/electrode junction is much less significant than that occurring at the bilayer heterojunction. Further, since the damage layer which occurs when, e.g., ITO, is deposited over an organic material is significant in causing exciton ionization, this damage may be controlled using the low power sputtering technique described in Parthasarathy Appl. '863. It is believed that controlling this damage region will insure that exciton ionization and carrier separation primarily occurs at the organic/organic bilayer heterojunction.--

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*Sub B*

Please replace the paragraph starting on page 30 at line 25 with the following paragraph:

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--An exemplary embodiment of a organic photosensitive optoelectronic cell with multiple organic layers, or a *multilayer* device 600, is shown in Fig. 6. Insulating or conducting substrate 601 supports the device. First electrode 602 comprises, e.g., ITO of approximate thickness 1000-4000 Å, preferably less than 2000 Å and most preferably around 1000 Å and is adjacent to first organic layer 603 comprising, e.g., PTCDA, PTCBI, or CuPc of approximate thickness 20-50 Å. A second organic layer 604 comprises, e.g., 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl ( $\alpha$ -NPD), approximately 200-500 Å in thickness, and is adjacent to first organic layer 603. A third organic layer 605, comprising, e.g., aluminum *tris*(8-hydroxyquinoline) (Alq<sub>3</sub>), approximately 200-500 Å in thickness, is adjacent to second organic layer 604 to form a rectifying heterojunction at the second organic layer 604 / third organic layer 605 interface. A fourth organic layer 606, comprising, e.g., CuPc, PTCBI, or PTCDA, of approximate thickness 20-50 Å is adjacent to third organic layer 605. Finally, second transparent electrode 607 is adjacent to the fourth organic layer 606 and comprises, e.g., ITO of approximate thickness 1000-4000 Å, preferably less than 2000 Å and most preferably around 1000 Å. In this embodiment, an extra pair of organic materials, here second organic layer 604 and third organic layer 605, selected to have appropriate relative mobilities and HOMO-LUMO offset for exciton ionization and charge separation is placed within a "sandwich" of two other organic materials, here first organic layer 602 and fourth organic layer 606. In this instance, the "inner" pair of organic materials, 604 and 605, provides the exciton ionization and charge separation and the "outer" pair, 603 and 606, serves both as charge transporting layers, i.e., transporting the separated carriers to the proper electrodes for substantially ohmic extraction, and as protective cap layers, i.e., protecting the inner pair of organic layers from damage during deposition and use. The outer pair of organic materials may be from the group consisting of CuPc, PTCDA, and PTCBI, or any two of the three may be used. That is, the same material or any combination thereof may be used for both contacts. Note, however, in embodiment 600, the interior pair of layers, 604

and 605, are preferably deposited so that the cathode side is on top so as to incorporate a low resistance cathode. However, as with the exemplary embodiment of Fig. 4A, the order of the deposition of the inner pair of organic materials is not critical electronically, though the order of the inner pair determines the polarity of the photosensitive optoelectronic device. Since the outer pair of organic layers is relatively thin, their electronic properties are of much less significance here than in the bilayer exemplary embodiment described herein above wherein the CuPc, PTCDA, and PTCBI also performed photoconversion and exciton ionization in addition to transporting the separated carriers. Accordingly, an alternate embodiment of the present invention (not depicted) in a multilayer device would include the cathode on the bottom. The inner pair of organic materials may each be an organic dye chosen to have photosensitivity in a desired region of the spectrum. Since the Alq<sub>3</sub> /  $\alpha$ -NPD pair is photosensitive in the ultraviolet (UV) part of the spectrum, multilayer device 600 with this organic pair combination is a particular exemplary embodiment of a UV photodetector. Further, the dye pair is preferably chosen to have a LUMO-HOMO gap offset as described above. In yet another embodiment (not shown) one or both of the outer pair of organic layers is replaced with a thin layer, approximately 50-150 Å of Mg:Ag alloy which acts as a charge transfer, extraction, and protective cap layer.--

Please replace the paragraph beginning on page 36 at line 3 with the following:

~~--A further embodiment of the present invention (not shown) is a variation of embodiment 900 and has the subcells separated by transparent insulating layers, such as SiO<sub>2</sub>, of approximate thickness 500-4000 Å, preferably less than 3000 Å and most preferably around 2000 Å, with additional transparent electrode layers as required in analogy to the unilayer and bilayer stacked devices described above. If the Alq<sub>3</sub> and  $\alpha$ -NPD layers are arranged with the Alq<sub>3</sub> on top then the subcells are all oriented with the cathode on top to utilize the low resistance cathode such as disclosed in Parthasarathy co-pending Appl. '707. With the subcells thus electrically isolated in the stack they may be connected externally in accord with the present invention in either a parallel or series manner as described with the bilayer subcells.--~~

Please replace the paragraph beginning at page 41 at line 31 with the following paragraph:

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-- In fabricating practical organic photosensitive optoelectronic devices, in addition to determining the optimal number of and thickness of layers to have in a stacked photosensitive optoelectronic device as discussed above, the area and arrangement of individual cells may be chosen to optimize efficiency and cost. Since the transparent electrodes that are to be used in these devices do have some residual absorption, it is preferable to keep such electrodes thin to minimize this absorption. In addition, keeping the electrode layers as thin as practicable minimizes fabrication time. On the other hand, as all electrode materials are made thinner, their sheet resistance increases. Therefore, it is preferable to minimize the distance which charge carriers must travel in the electrode after collection. A configuration which maximizes photosensitive optoelectronic receptive area and accomplishes this goal is one in which the devices are laid out in long strips on the substrate with electrical connection made to the devices electrodes along the longer sides. U.S. Patent Application Serial No. 04/976,666 to Forrest et al. (hereinafter Forrest Appl. '666), which is incorporated herein by reference in its entirety, describes techniques for fabrication of practical organic thin film devices.--

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Please replace the paragraph beginning on page 42 at line 16 with the following paragraph:

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-- Parthasarathy Appl. '707 disclosed that small molecular organic materials with relatively large planar molecules and a highly conjugated structure, such as CuPc and PTCDA, are believed to be able to withstand energetic electrode deposition because of the highly delocalized nature of their bonding which spreads the energy of impact over more than one bond. When an energetic metal or oxygen atom is incident on one of these molecules at a surface during sputtering, the energy of impact is thought to be efficiently distributed over the numerous bonds in the molecular  $\pi$ -electron systems. In contrast, no comparably large  $\pi$ -electron systems exist in, e.g., Alq<sub>3</sub> or  $\alpha$ -NPD. For such molecules, the impact energy is more localized among only a few atomic sites, thereby increasing the probability for breaking a

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molecular bond. The planar or nearly planar stacking arrangements of crystalline molecular systems such as CuPc and PTCDA may also assist in the dissipation of energy among several neighboring molecules in the lattice. Accordingly, it is believed that the low resistance non-metallic cathode such as disclosed in Parthasarathy Appl. '707 can also be embodied in other similar types of small molecular crystals. For example, CuPc may be replaced by other metal phthalocyanines, naphthalocyanines and porphyrins. PTCDA may be replaced for example by other polyacenes. Some other representative photosensitive optoelectronic small molecule organic heterostructure combinations contemplated as suitable for use in accord with the present invention are shown in Table 1.--

Please replace the paragraph beginning on page 45 at line 1 with the following paragraph:

--Also, it will be appreciated that the novel concept of electrically connecting organic photosensitive optoelectronic devices in parallel to overcome the inefficiencies associated with their high series resistance and related space charge effects is equally applicable to other organic photosensitive optoelectronic devices comprising other subcell compositions.

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Similarly the novel concept of connecting stacked organic photosensitive optoelectronic devices in series with external connections to intervening electrodes to provide a multivoltage power supply is applicable to other organic photosensitive optoelectronic devices. Also, use of the low resistance non-metallic cathode disclosed in co-pending Parthasarathy Appl. '707 in place of a traditional semi-transparent metallic cathode, such as disclosed in prior art organic photosensitive optoelectronic material configurations, is intended to be within the scope of the present invention.--

**In the Claims:**

Please cancel pending claims 1-53 as originally filed, and add new claims 54-74 as follows: